HHS Public Access

Author manuscript

Macromolecules. Author manuscript; available in PMC 2016 June 09.

Published in final edited form as:

Macromolecules. 2015 June 9; 48(11): 3788–3801. doi:10.1021/acs.macromol.5b00586.

Strong Selective Adsorption of Polymers

Ting Ge and **Michael Rubinstein***

Department of Chemistry, University of North Carolina, Chapel Hill, North Carolina 27599-3290, United States

Abstract

A scaling theory is developed for selective adsorption of polymers induced by the strong binding between specific monomers and complementary surface adsorption sites. By "selective" we mean specific attraction between a subset of all monomers, called "sticky", and a subset of surface sites, called "adsorption sites". We demonstrate that, in addition to the expected dependence on the polymer volume fraction φ_{bulk} in the bulk solution, selective adsorption strongly depends on the ratio between two characteristic length scales, the root-mean-square distance l between neighboring sticky monomers along the polymer, and the average distance d between neighboring surface adsorption sites. The role of the ratio l/d arises from the fact that a polymer needs to deform to enable the spatial commensurability between its sticky monomers and the surface adsorption sites for selective adsorption. We study strong selective adsorption of both telechelic polymers with two end monomers being sticky and multisticker polymers with many sticky monomers between sticky ends. For telechelic polymers, we identify four adsorption regimes at $l/d < 1$ that are characterized by the fraction of occupied adsorption sites and whether the dominant conformation of adsorbed chains is a single-end-adsorbed "mushroom" or double-end-adsorbed loop. For $l/d > 1$, we expect that the adsorption layer at exponentially low φ_{bulk} consists of separated unstretched loops, while as φ_{bulk} increases the layer crosses over to a brush of extended loops with a second layer of weakly overlapping tails. For multisticker chains, in the limit of exponentially low φ_{bulk}, adsorbed polymers are well separated from each other. As l/d increases, the conformation of an individual polymer changes from a single-end-adsorbed "mushroom" to a random walk of loops. For high φ_{bulk}, adsorbed polymers at small l/d are mushrooms that cover all the adsorption sites. At sufficiently large l/d, adsorbed multisticker polymers strongly overlap. We anticipate the formation of a self-similar carpet and with increasing l/d a two-layer structure with a brush of loops covered by a self-similar carpet. As l/d exceeds the threshold determined by the adsorption energy, the brush of loops under the carpet reaches a saturated state, resulting in a l/d-independent brush-under-carpet structure, which can also be applied to describe adsorbed multisticker polymers in nonselective adsorption where a sticker can strongly bind to any place on the adsorption surface. We examine the adsorbed amount Γ of multisticker polymers in different regimes for selective adsorption. If the adsorbed multisticker polymers are nonoverlapping mushrooms, the adsorbed amount Γ increases linearly with the surface density of adsorption sites

***Corresponding Author:**mr@unc.edu (M.R.).

Supporting Information

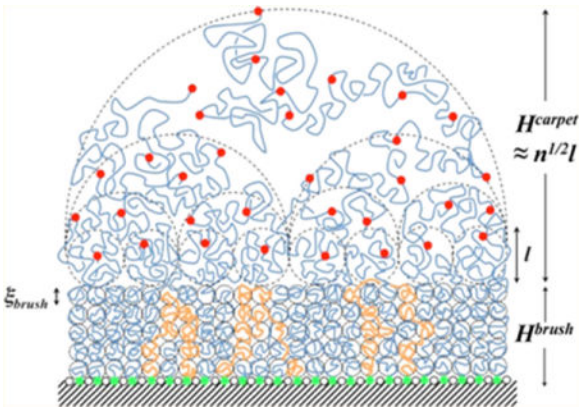
The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.macro-mol.5b00586.

Notes

The authors declare no competing financial interest.

$\Sigma \approx 1/d^2$. In the self-similar carpet regime, Γ increases sublinearly as $\Sigma^{0.15}$ in a good solvent, while only logarithmically in a theta solvent. Formation of a brush layer under the carpet contributes an additional adsorbed amount. This additional amount increases linearly with Σ and eventually dominates the overall adsorbed amount Γ before saturating at a plateau value controlled by the adsorption energy.

Graphical abstract



1. INTRODUCTION

Surface adsorption of polymers is a classical problem in polymer physics and is also a subject of great technological importance.[1] One scenario that has been widely studied[2–9] is weak adsorption, where the adsorption energy per monomer is small compared with the thermal energy but the overall adsorption energy for the whole polymer is large. Multiple polymers bind to a weakly adsorbing surface from a solution and build an adsorption layer. In the limit of very dilute solution, the surface coverage is low with no overlap of adsorbed polymers. Therefore, the adsorption process can be understood by studying the adsorption of a single polymer chain.[2] The conformation of an adsorbed polymer is a two-dimensional array of adsorption blobs of size ξ_{ads}. The adsorption blob size ξ_{ads} and hence the height of the adsorbed polymer is determined by the balance between the entropic loss due to the chain confinement near the adsorption surface and the energetic gain from polymer–surface interactions. In contrast, adsorbed polymers at high surface coverage strongly overlap with each other. It is well established that the weak adsorption layer of overlapping chains can be described as a self-similar carpet.[5,7] As originally argued by de Gennes,[5,7] the correlation length ξ in the adsorbed polymer layer scales linearly with the distance z to the adsorption surface. The volume fraction profile of monomers constructed accordingly has a self-similar form as a function of z. In the case of adsorption under good solvent conditions, most monomers are confined in a narrow region close to the surface, in which the entropic penalty due to repulsion between chain sections is balanced by the energetic gain from adsorption. The thickness of this region is on the oder of the same adsorption blob size ξ_{ads} as in the single-chain weak adsorption. However, as demonstrated by Scheutjens and Fleer's calculation based on a statistical lattice model[3,4] and Semenov and Joanny's scaling analysis,[9] the adsorbed chains consist of loops and tails of various sizes, which dominate the inner and outer parts of the adsorption layer, respectively. Therefore, the thickness of the

entire layer adsorbed from dilute solution is controlled by the size of dangling loops and tails and scales with the unperturbed size of the whole chain.

Adsorption of polymers carrying strongly adsorbing terminal monomers has also been investigated.[10–14] Adsorbed polymers with a single adsorbing terminal monomer are well separated from each other at exponentially low polymer volume fractions, forming so-called “mushrooms”. However, they strongly overlap at high volume fractions, resulting in brush-like structures where chains are extended normal to the adsorption surface. Based on the scaling descriptions by Alexander[10] and de Gennes,[11] an adsorbed chain in the brush can be approximated as a stretched array of correlation blobs whose size is on the order of the average distance between adsorbed chains. The repulsion of a chain from its neighbors in the brush $\approx k_B T$ times the number of correlation blobs per chain is balanced by the energy gain $\approx \delta k_B T$ ($\delta \gg 1$) from the adsorption of chain end to the surface. As a result, the height of extended chains depends on the molecular weight of the polymer and the adsorption strength characterized by δ.

In the present paper, we study selective adsorption of polymers induced by the strong binding of specific monomers along the polymer and complementary adsorption sites on a surface. One example is the adsorption of weakly charged polyelectrolytes onto an oppositely and sparsely charged surface,[15–19] where charges of opposite signs strongly bind to each other, forming ionic pairs. This process is essential to the first step of the layer-by-layer assembly of thin polyelectrolyte films.[18,19] Strong attraction can also be realized through the ligand–receptor interactions. Recently, the adsorption of polymers grafted with multiple ligands onto a surface covered by receptors has attracted wide interest,[20–24] as it underlies cell surface recognition, and can be potentially utilized to design self-assembling materials for therapeutic delivery.

We develop a scaling theory for the equilibrium structure of strongly and selectively adsorbed polymers. In our model, the monomers that can be bound to surface adsorption sites are called “sticky”. The difference between “sticky” monomers and other monomers is the origin of selectivity in our adsorption model. Note that selective adsorption in this paper does not necessarily indicate selectively adsorbing specific polymers out of all solution polymers. Two important length scales, the root-mean-square distance l between neighboring sticky monomers along the polymer in dilute solutions and the average distance d between neighboring adsorption sites at the surface, affect the adsorption behavior. Depending on the ratio l/d and the volume fraction φ_{bulk} of polymers in the bulk solution, adsorbed chains assume different conformations at the surface. For small l/d, the polymer needs to elongate to reach neighboring adsorption sites. The competition between the stretching free energy and the adsorption energy determines the favorable conformations of adsorbed polymers. For large l/d, chain stretching is not necessary for adsorption. However, the adsorbed polymers can be at high volume fraction with strong overlap and repulsion from each other, which imposes a free energy penalty. The balance of the repulsion between overlapping chains and the adsorption energy controls the structure of the adsorbed polymer layer.

Marques and Joanny[25] have studied the adsorption of copolymers in which one type of monomers (stickers) regularly distributed along the chain can be strongly bound to adsorption sites uniformly distributed on a surface. The model they used for copolymer adsorption is similar to our model for the strong selective adsorption of polymers. However, in their study of the multichain adsorption from a dilute copolymer solution, Marques and Joanny focused on only one regime in which the average spacing d between surface adsorption sites is much smaller than the average distance l between neighboring stickers along the polymer chain, i.e., $l/d \gg 1$. Furthermore, they assumed that the binding strength between a sticker and an adsorption site is sufficiently large so that all the adsorption sites are occupied by stickers. In contrast, we systematically examine the dependence of the strong selective adsorption behavior on the ratio l/d. We also show that there is a δ-dependent threshold value of the ratio l/d above which only a fraction of the adsorption sites are occupied and the adsorption layer reaches an equilibrium structure independent of the ratio l/d. Marques and Joanny proposed a scaling model of the layer formed by copolymers adsorbed from a dilute solution. On the basis of the self-similar carpet model for the weak adsorption of homopolymers and the brush model for densely end-grafted homopolymers, they described the adsorption layer of copolymers as a structure intermediate between a self-similar carpet and a brush, containing loops of varying sizes with both ends bound to the adsorption surface via stickers. This scaling model is analogous to, but somewhat different from, the one we construct for the layer of strongly and selectively adsorbed polymers each carrying multiple sticky monomers with the ratio $l/d > 1$. We shall compare the two models and demonstrate that ours is thermodynamically favorable.

The ratio of the distance between specific monomers that can be adsorbed to a surface and the spacing between complementary adsorption surface sites has been identified as an important factor controlling the adsorption of copolymers onto a surface containing two types of adsorption sites for the two species of monomers in the copolymer.[26–29] For block copolymers that have an ordered sequence of monomers along the chain, the adsorbed amount of polymers is higher for a patchwise surface with adsorption sites of the same type grouped together compared to a surface with randomly distributed adsorption sites.[26] In contrast, for random copolymers with a disordered monomer sequence, a single chain strongly adsorbs onto a surface if the distribution pattern of the adsorption sites closely matches the random sequence of monomers.[27–29]

Previous studies[16,17,19] of other polymer adsorption problems have taken into account the free energy associated with the entropy of the loops connecting adsorption sites on the adsorption surface. In his study of the adsorption of a partially charged polymer to a surface with an oppositely charged pattern, Muthukumar[16,17] examined the loops linking ionic pairs on the adsorption surface at different stages of the adsorption process and demonstrated that the entropic free energy penalty arising from the stretching of these loops affects the kinetics of adsorption. For fully charged polyelectrolyte chains adsorbed on a surface with uniformly distributed opposite charges, Lefaux et al.[19] described the adsorption layer as a brush of loops extended normal to the adsorption surface and determined the equilibrium height of the brush layer through balancing the extension free energy of the loops and the free energy terms due to electrostatic interaction.

Our scaling theory predicts the equilibrium structure of strongly and selectively adsorbed polymers in various regimes based on the analysis of the free energy of the adsorbed polymers. Section 2 presents results for telechelic polymers with only two sticky monomers. Section 3 deals with multisticker polymers containing multiple sticky monomers. Results are summarized in section 4.

2. SELECTIVE ADSORPTION OF TELECHELIC POLYMERS

Consider telechelic polymers, each consisting of q Kuhn monomers of size b with the end monomers being sticky, in a solution contacting an adsorption surface with the average distance d between adsorption sites. Each sticky monomer (S) is allowed to bind to at most one adsorption site (A). The adsorption energy for the binding between a sticky monomer and an adsorption site (S + A $\rightarrow$ SA) is

$$\varepsilon_{\mathrm{ads}} \approx -\delta k_{\mathrm{B}} T \quad (1)$$

which is much stronger than the thermal energy $k_{\mathrm{B}}T$ with $\delta \gg 1$. Note that the number of conformations an isolated polymer containing q monomers with one end bound to the surface, a so-called “mushroom”, can adopt is reduced with respect to the corresponding number of chain conformations of an ideal Gaussian random coil away from the hard-wall surface by a factor $\approx q^{-1/2}$ (proximity effect).[30,31] To overcome the free energy penalty $\approx k_{\mathrm{B}}T\ln q \approx k_{\mathrm{B}}T$ associated with the conformational entropy loss in the proximity of the surface and induce the desorption–adsorption transition, a critical adsorption energy $\varepsilon_{\mathrm{cr}} \approx k_{\mathrm{B}}T$ is needed.[30–32] Therefore, the adsorption energy gain $\delta k_{\mathrm{B}}T$ in our scaling theory should be considered as the free energy gain in excess of the critical energy $\varepsilon_{\mathrm{cr}}$, which is a small correction for $\delta \gg 1$.

The root-mean-square distance between sticky monomers at chain ends of a telechelic polymer is

$$l \approx q^{1/2} b \quad (2)$$

for the unabsorbed chains in a theta solution. Here and below, we shall base our discussion on the results for a theta solvent. Results for an athermal solvent are presented and compared with those for a theta solvent in section F of the Supporting Information. Additionally, we ignore any order-unity prefactors throughout the paper while focusing on the scaling relations and use the sign $\approx$ to indicate equality on the scaling level up to a numerical coefficient of order unity.

2.1. Adsorption of a Single Telechelic Polymer

The conformation of a single adsorbed telechelic polymer depends on the ratio between its size l in dilute solution and the average spacing d between adsorption sites. For $l/d < 1$, a telechelic polymer can either adsorb to one site or stretch to occupy two neighboring adsorption sites. Through occupying the second adsorption site, the free energy of the chain is further reduced by

$$f_{\text{gain}} \approx |\varepsilon_{\text{ads}}| \approx \delta k_{\text{B}} T \quad (3)$$

However, there is an entropic penalty

$$f_{\text{penalty}}^{\text{loop}} \approx k_{\text{B}} T d^2 / l^2 \quad (4)$$

associated with this chain stretching relative to the unperturbed size l. The competition between the additional energetic gain f_{gain} and the entropic loss $f_{\text{penalty}}^{\text{loop}}$ due to stretching determines whether the favorable chain conformation is a stretched loop with two ends absorbed or a mushroom with only one end adsorbed. For $l/d < \delta^{-1/2} < 1$, the entropic penalty from stretching dominates over the additional energetic gain $\left(f_{\text{penalty}}^{\text{loop}} > f_{\text{gain}}\right)$. As a result, the favorable conformation is a mushroom as illustrated in the left panel of Figure 1 (regime I). In contrast, for $\delta^{-1/2} < l/d < 1$, the additional energetic gain is able to overcome the entropic penalty $\left(f_{\text{gain}} > f_{\text{penalty}}^{\text{loop}}\right)$. The favorable telechelic conformation is a stretched loop as shown in the middle panel of Figure 1 (regime II). For $l/d > 1$, no stretching is needed for a single polymer to occupy two adsorption sites. A polymer assumes the conformation of an unstretched loop with its two ends bound to the surface. This scenario is illustrated in the right panel of Figure 1 (regime III).

2.2. Multichain Adsorption of Telechelic Polymers for *l*/*d* < 1

The adsorption behavior of multiple polymers is affected by the volume fraction φ_{bulk} of polymers in the bulk solution away from the adsorption surface. The role of φ_{bulk} is related to the translational entropy of polymers, which is $-k_{\text{B}} \ln \varphi_{\text{bulk}}$ per chain in the bulk solution. As a polymer leaves the bulk solution and becomes bound to one or two adsorption sites, its translational entropy is reduced. In the limit of low bulk volume fraction φ_{bulk}, this free energy penalty from entropy loss is comparable to other terms in the overall free energy change upon adsorption, and therefore adsorption sites are partially covered to avoid the additional translational entropy loss due to adsorbing more chains. Essentially, the bulk volume fraction φ_{bulk} sets up the chemical potential of chains in the bulk solution

$$\mu \approx k_{\text{B}} T \ln \phi_{\text{bulk}} \quad (5)$$

For $l/d < 1$, as in the adsorption of a single telechelic polymer, we need to consider two possible chain conformations: a mushroom and a stretched loop. Depending on the volume fraction φ_{bulk} and the ratio l/d, there are four adsorption regimes, as schematically shown in Figure 2. Regimes separated by the blue line differ in the fraction θ of adsorption sites occupied by sticky monomers. In regimes I and II, the surface is sparsely covered with $\theta \ll 1$, whereas in regimes III and IV, most of the surface adsorption sites are covered with $\theta > 1/2$. Regimes on two sides of the red line are distinguished by the dominant conformation of adsorbed chains. On the left side of the red line (regimes I and III), a higher fraction of adsorption sites are occupied by mushrooms. On the right side (regimes II and IV), the dominant conformation is a stretched loop. Section A of the Supporting Information gives

the derivation of the two boundary lines (blue and red lines) in the left part ($l/d < 1$) of Figure 2. Below we discuss the physical meanings of these crossovers.

In the mushroom-dominant regimes I and III, the bulk polymer volume fraction φ_{bulk} at the crossover between low and high coverage of adsorption sites is along the blue boundary line $\sim e^{-\delta}$. This result can be understood based on the classical adsorption theory,[33] according to which the fraction of surface adsorption sites occupied by mushrooms is

$$\theta \approx 1/\left[e^{-(\mu-\varepsilon_{\text{ads}})/k_{\text{B}}T}+1\right], \quad \text{for } l/d<\delta^{-1/2} \quad (6)$$

More than half of the adsorption sites are occupied ($\theta > 1/2$) if the chemical potential μ of polymer chains is larger than the adsorption energy per chain, which is equal to the adsorption energy per site ε_{ads} because only one sticky monomer per chain is adsorbed in the mushroom conformation. Using eq 1 for ε_{ads} and eq 5 for μ, we obtain $\varphi_{\text{bulk}} > e^{-\delta}$ as the condition for high surface coverage by mushrooms with $\theta > 1/2$.

In the loop-dominant regimes II and IV, the effective adsorption energy per chain is

$$\varepsilon_{\text{ads}}^{\text{eff}} \approx -2f_{\text{gain}}+f_{\text{penalty}}^{\text{loop}} \approx -2\delta k_{\text{B}}T+k_{\text{B}}Td^2/l^2 < -\delta k_{\text{B}}T \quad (7)$$

where the first term is the energetic gain from the adsorption of two sticky monomers and the second one is the entropic penalty due to chain stretching. Grouping two adjacent adsorption sites into one effective site for the adsorption of a stretched loop, and replacing ε_{ads} in eq 6 with the effective adsorption energy $\varepsilon_{\text{ads}}^{\text{eff}}$ per loop, we obtain that the fraction θ^{eff} of effective adsorption sites occupied by stretched loops and thus the fraction of occupied adsorption sites

$$\theta \approx \theta^{\text{eff}} \approx 1/\left[e^{-\left(\mu-\varepsilon_{\text{ads}}^{\text{eff}}\right)/k_{\text{B}}T}+1\right], \quad \text{for } \delta^{-1/2} < l/d < 1 \quad (8)$$

which at constant bulk volume fraction φ_{bulk} increases with the ratio l/d due to the increase in the adsorption strength per chain $|\varepsilon_{\text{ads}}^{\text{eff}}| = -\varepsilon_{\text{ads}}^{\text{eff}}$. The crossover bulk volume fraction φ_{bulk} on the blue boundary line ($\theta \approx 1/2$) between low and high coverage of adsorption sites, which scales as $\sim e^{\varepsilon_{\text{ads}}^{\text{eff}}/k_{\text{B}}T} = e^{-|\varepsilon_{\text{ads}}^{\text{eff}}|/k_{\text{B}}T}$, decreases with l/d. At $l/d \approx 1$, the effective adsorption energy $\varepsilon_{\text{ads}}^{\text{eff}} \approx -2\delta k_{\text{B}}T$ because there is almost no chain stretching $\left(f_{\text{penalty}}^{\text{loop}} \approx 0\right)$, and the crossover bulk volume fraction is $\varphi_{\text{bulk}} \approx e^{-2\delta}$ as indicated in Figure 2.

The boundary between regimes I and II at low bulk volume fraction φ_{bulk} approaches $l/d \approx \delta^{-1/2}$, which is the same condition that determines the boundary between regimes I and II for the adsorption of a single telechelic polymer (see Figure 1). In fact, since only a small fraction of surface adsorption sites are covered in the limit of low φ_{bulk}, the adsorption process is essentially identical to that of a single polymer.

For sufficiently high polymer volume fraction φ_{bulk}, the adsorption sites are almost fully covered by either loops or mushrooms. Formation of loops introduces entropic penalty associated with chain stretching, while covering adsorption sites by mushrooms results in

higher translational entropy loss because one loop has to be replaced by two mushrooms, and hence twice as many chains need to be bound to the surface to achieve the same high coverage of adsorption sites. For loops, the free energy penalty per site from stretching is $f_{\text{penalty}}^{\text{loop}} \approx k_{\text{B}}Td^2/l^2$ (eq 4). For mushrooms, the penalty per site from additional translational entropy loss is

$$f_{\text{penalty}}^{\text{mushroom}} \approx -k_{\text{B}}T \ln \phi_{\text{bulk}} \quad (9)$$

If $f_{\text{penalty}}^{\text{mushroom}} < f_{\text{penalty}}^{\text{loop}}$, high coverage of the surface by mushrooms is more favorable. Otherwise, the favorable conformation is a stretched loop. As a result, from $f_{\text{penalty}}^{\text{mushroom}} \approx f_{\text{penalty}}^{\text{loop}}$, the boundary between loop-dominant and mushroom-dominant regimes is $\phi_{\text{bulk}} \approx \text{e}^{-d^2/l^2}$ bulk for bulk volume fraction $\varphi_{\text{bulk}} > \text{e}^{-\delta}$ with high adsorption site coverage. As indicated by the red line in Figure 2, the boundary between mushroom-dominant and loop-dominant regimes starts at $l/d \approx \delta^{-1/2}$ for exponentially low bulk volume fraction $\varphi_{\text{bulk}} < \text{e}^{-\delta}$ and bends toward higher l/d with increasing φ_{bulk} as $l/d \sim (-\ln \varphi_{\text{bulk}})^{-1/2}$

2.3. Multichain Adsorption of Telechelic Polymers for l/d > 1

If the root-mean-square end-to-end distance l of telechelic polymers in the solution is larger than the average spacing d between adsorption sites, both ends of a telechelic polymer can adsorb onto the surface without stretching. At exponentially low bulk volume fraction $\varphi_{\text{bulk}} < \text{e}^{-2\delta}$, the adsorption site coverage is low and adsorbed polymers do not overlap with each other. Each adsorbed polymer assumes the conformation of an unstretched loop with the two sticky end monomers both adsorbed to the surface. Note that once a chain is adsorbed at one end, there are plenty of adsorption sites available for the other end. For strong adsorption with $\delta \gg 1$, the energetic gain from having the other end also adsorbed far exceeds the entropic penalty of forming a loop to enable the adsorption of the other end. Therefore, at thermal equilibrium, the fraction of polymers with only one end adsorbed is exponentially low ($\approx \text{e}^{-\delta}$) and thus can be ignored.

As the bulk volume fraction φ_{bulk} becomes sufficiently high, adsorbed polymers overlap. The overlap condition can be estimated as follows. As in the Langmuir model for the adsorption of ideal gas,[33] one can divide the adsorption surface into adsorption regions with dimensions on the order of the unstretched loop size l. Each adsorption region can be occupied by one polymer in the conformation of an unstretched loop with adsorption energy $\varepsilon_{\text{ads}}^{\text{loop}}$. The fraction of occupied adsorption regions

$$\eta \approx 1/\left[\text{e}^{-\left(\mu-\varepsilon_{\text{ads}}^{\text{loop}}\right)/k_{\text{B}}T}+1\right], \quad \text{for } l/d>1 \quad (10)$$

Note that eqs 6, 8, and 10 have identical mathematical forms due to the application of the same Langmuir adsorption model.[33] The fraction θ of occupied adsorption sites for $l/d < 1$ and the fraction η of occupied adsorption regions for $l/d > 1$ match each other at $l/d = 1$, where the surface area per adsorption sites d^2 is equal to the area l^2 of an adsorption region.

Overlap of adsorbed polymers for $l/d > 1$ begins if almost all adsorption regions of size l^2 are occupied, i.e., as unstretched loops fill up the surface. According to eq 10, occupation of the majority ($\eta > 1/2$) of the adsorption regions occurs if the chemical potential μ of polymers is higher than the adsorption energy per chain. Using eq 5 for μ and the adsorption energy per unstretched loop $\varepsilon_{\text{ads}}^{\text{loop}} \approx -2\delta k_{\text{B}}T$ due to two adsorbed sticky end monomers, we obtain the estimated condition $\varphi_{\text{bulk}} > e^{-2\delta}$ for the occupation of most adsorption regions and hence the overlap of adsorbed unstretched loops. Within the surface area $\approx l^2$ of an adsorption region covered by an unstretched loop, two out of $\approx l^2/d^2$ adsorption sites are occupied, corresponding to a fraction $\approx d^2/l^2 < 1$. Therefore, at the overlap of unstretched loops with $\eta \approx 1$, the fraction of occupied adsorption sites $\theta^{\text{overlap}} \approx \eta(d^2/l^2) \approx d^2/l^2 < 1$. The blue line in the right part ($l/d > 1$) of Figure 2 indicates the crossover bulk volume fraction $\varphi_{\text{bulk}} \approx e^{-2\delta}$ for adsorbed polymers in the conformation of unstretched loops to overlap. Note that this line is a continuation of the boundary line between low and high coverage regimes at $l/d < 1$.

Repulsion between overlapping polymers (three-body repulsion in a theta solvent and two-body repulsion in a good solvent) forces them to extend away from the adsorption surface, forming a brush layer. Extension of the chains relative to the unpertubed size of isolated random coils reduces the conformational entropy of the chains and thereby increases the free energy of the adsorption layer. The repulsion energy is on the order of $k_{\text{B}}T$ per correlation blob of size ξ, while the extension free energy is on the order of $k_{\text{B}}T$ per tension blob of size ξ_{t}. At equilibrium, the osmotic pressure $\approx k_{\text{B}}T/\xi^3$ from repulsion between polymers and the tensile stress $\approx k_{\text{B}}T/\xi_{\text{t}}^3$ from extension of polymers balance each other, resulting in $\xi_{\text{t}} \approx \xi$. Therefore, the overall interaction free energy at equilibrium, including the repulsion energy between chains and their extension free energy, is on the order of $k_{\text{B}}T$ per correlation blob of size ξ. At adsorption site coverage θ, the correlation blob size ξ in the brush, which is the average distance between sections of neighboring chains, is larger than the average spacing d between adsorption sites by a factor $\theta^{-1/2}$.

$$\xi \approx d/\theta^{1/2} \quad (11)$$

The number of monomers in one correlation blob of size ξ is

$$g \approx \xi^2/b^2 \approx d^2/\left(\theta b^2\right) \quad (12)$$

while the number of correlation blobs per chain is

$$p \approx q/g \approx \theta l^2/d^2 \quad (13)$$

Since the interaction free energy is $\approx k_{\text{B}}T$ per correlation blob, the interaction free energy per chain in the brush is

$$\varepsilon_{\text{brush}} \approx pk_{\text{B}}T \approx k_{\text{B}}T\theta l^2/d^2 \quad (14)$$

At the same adsorption site coverage θ, a brush formed by extended loops with two ends adsorbed is more favorable than a brush formed by extended tails with only one end adsorbed. The two brushes gain the same amount of free energy from binding to the same number of surface adsorption sites. However, the interaction free energy of all the adsorbed chains in the brush of extended loops is only half of the interaction free energy for the brush of extended tails because while the interaction free energy per chain in the brush $\varepsilon_{brush} \approx k_B T\theta l^2/d^2$ is identical for the two brushes, only half as many loops as tails are adsorbed at the same coverage θ. (Alternatively, one can see this by noting that the brush of tails is twice higher than the brush of loops at the same surface density θ/d^2 of occupied adsorption sites while the interaction free energy density is $\approx k_B T/\xi^3$ in both brushes.) As a result, the overall free energy of adsorbed chains is lower for the brush of extended loops, making it thermodynamically more favorable.

Nevertheless, a mixture of extended loops and open chains with tails as illustrated in Figure 3 is even more favorable than the pure state of a brush formed exclusively by extended loops because of the additional free energy gain arising from the mixing entropy. Note that an extended loop with two adsorbed sticky ends is completely located in the brush layer (see the orange chain in Figure 3). In contrast, for an open chain with one sticky end adsorbed, only half of the chain is embedded in the brush with the other half, the tail, staying above the brush (see cyan chains in Figure 3). Starting from the brush of extended loops, the mixing entropy increases as more loops open up to form tails. However, before it reaches the maximum value, the tails above the brush start to overlap and repel each other, resulting in free energy penalty. Since the mixing entropy per chain is $k_B T$ times a logarithmic term, it can be easily suppressed by the free energy penalty from the strong overlap of tails, which is multiple times $k_B T$ per chain. Therefore, tails weakly overlapping with each other optimize the structure of adsorbed telechelic chains. Such a layer of tails is schematically shown in Figure 3. Section B of the Supporting Information gives a detailed calculation demonstrating that a brush of loops with weakly overlapping tails above it is the favorable structure of the adsorbed telechelic polymers.

The equilibrium structure of the adsorbed brush layer in the limit of high bulk volume fraction φ_{bulk} can be determined by evaluating the free energy gain from adsorption and the interaction free energy of chains in the brush. In a solution with high polymer volume fraction φ_{bulk} and therefore high chemical potential, polymers try to occupy as many as possible adsorption sites to lower the free energy. If almost all the adsorption sites are occupied, i.e., adsorption site coverage $\theta \approx 1$, the interaction free energy per chain in the brush $\varepsilon_{brush} \approx k_B T l^2/d^2$ based on eq 14. For $l/d < \delta^{1/2}$, this interaction free energy per chain ε_{brush} is smaller than the energetic gain $\sim \delta k_B T$ per chain from adsorption. As a result, coverage of almost all adsorption sites can be realized. This corresponds to regime VI in Figure 2. In this regime the correlation length in the brush $\xi \approx d$ is set by the average distance d between adsorption sites (see eq 11 with $\theta \approx 1$).

For higher value of the ratio $l/d > \delta^{1/2}$, corresponding to regime VII in Figure 2, the interaction free energy per chain in the brush $\varepsilon_{brush} \approx k_B T l^2/d^2$ at almost full coverage of adsorption sites exceeds the energetic gain per chain $\approx \delta k_B T$ from adsorption. As a result, occupying almost all adsorption sites is unfavorable, and polymers can only occupy a

fraction of adsorption sites. The balance of the interaction free energy $\varepsilon_{brush} \approx k_B T\theta l^2/d^2$ (eq 14) and the adsorption energy gain $\delta k_B T$ yields that at equilibrium the coverage of adsorption sites is $\theta \approx \delta d^2/l^2 < 1$ and from eq 11 the correlation length in the brush $\xi \approx l/\delta^{1/2}$, which is controlled by the adsorption strength δ and independent of the average spacing d between adsorption sites as indicated in Figure 3.

The height H of the brush roughly equals the length of a stretched array of p correlation blobs along the chain. Using eq 11 for the correlation blob size ξ and eq 13 for the number p, we get

$$H \approx p\xi \approx \theta^{1/2} l^2/d \quad (15)$$

In regime VI with almost full adsorption sites coverage $\theta \approx 1$, this height of adsorbed brush $H \approx l^2/d$ increases with l/d. However, in regime VII with coverage $\theta \approx \delta d^2/l^2$, the brush height $H \approx l\delta^{1/2}$ saturates at a constant value determined by the adsorption strength δ independent of the average spacing d between adsorption sites. Moreover, the height of the entire adsorption layer $H + l$ in regime VII is dominated by the brush height H, since the thickness of the second layer of tails at overlap with each other is on the order of l, which is much smaller than the brush height $H \approx l\delta^{1/2}$.

The adsorbed amount Γ defined as the number of monomers in the adsorbed telechelic polymers per unit area is

$$\Gamma \approx q/\xi^2 \approx \theta q/d^2 \quad (16)$$

where we used eq 11 for ξ. Note that both loops with two end monomers adsorbed and open chains with only one end adsorbed are counted as adsorbed polymers. In regime VI, the adsorbed amount $\Gamma \approx q/d^2 \approx (l/d)^2/b^2$ increases with the ratio l/d, whereas in regime VII, the adsorbed amount saturates at the maximum coverage $\Gamma \approx q\delta/l^2 \approx \delta/b^2$ determined by the adsorption strength δ. Note that regime VII with $l/d > \delta^{1/2}$ is equivalent to strong nonselective adsorption of telechelic polymers in which specific groups at chain ends can adsorb to any place on the adsorption surface with strong free energy gain that is $\delta k_B T \gg k_B T$ per adsorbed group.

3. SELECTIVE ADSORPTION OF MULTISTICKER POLYMERS

Consider a chain consisting of $n + 1$ sticky monomers separated by n linking segments, each of which contains on average $q - 1 \approx q$ monomers. In a theta solvent, the average spacing between neighboring sticky monomers or the root-mean-square end-to-end distance of a linking segment is $l \approx bq^{1/2}$, and the ideal size of multisticker polymers containing $(n + 1) + n(q - 1) \approx nq$ monomers is $b(nq)^{1/2} \approx n^{1/2} l$.

3.1. Adsorption of a Single Multisticker Polymer

A multisticker polymer tries to occupy as many surface adsorption sites as possible at minimal extension to lower its free energy. For a surface with densely distributed adsorption sites, all sticky monomers of the polymer can easily find an adsorption site to occupy with the linking segments between adsorbed sticky monomers remaining unstretched. However,

for a sparse distribution of adsorption sites, the polymer has to stretch to allow sticky monomers to reach adsorption sites, resulting in entropic free energy penalty. As a consequence, the balance between the energetic gain from adsorption and the entropic loss from chain stretching determines the optimized number of adsorbed sticky monomers and the equilibrium conformation of the whole chain. Below we examine the conformation of a single adsorbed multisticker polymer in different ranges of l/d.

3.1.1. Regime I: Mushroom—In the limit of very small $l/d < n^{-1/2}\delta^{-1/2}$, corresponding to very sparse distribution of adsorption sites, the polymer adopts the conformation of a random coil with one sticky monomer adsorbed, resembling a mushroom as illustrated in regime I in Figure 4. (Note that the probability of the adsorbed sticky monomer being at chain end is higher than that of being in the interior of the chain, as the proximity effect is weaker at chain ends.) No other sticky monomer is adsorbed because that would require very strong stretching of the polymer with the resulting entropic free energy penalty $\approx k_B T d^2/(nl^2)$ higher than the energetic gain $\approx k_B T\delta$ from the second adsorption. In this regime, both the size $R_\backslash$ of the adsorbed chain along the adsorption surface and the chain size $R_\perp$ normal to the surface are on the order of the ideal size $n^{1/2}l$ of chains in the bulk solution.

3.1.2. Regimes II and III: Random Walks of Stretched Loops—For higher ratio $l/d > n^{-1/2}\delta^{-1/2}$, the polymer can occupy more than one adsorption site. Suppose m sticky monomers are adsorbed, then successive segments containing $nq/(m-1)$ monomers along the chain are stretched along the surface to form loops connecting m adsorption sites. The unstretched size of such a loop is

$$s \approx \left(\frac{nq}{m-1}\right)^{1/2} b \approx \left(\frac{n}{m-1}\right)^{1/2} l \quad (17)$$

and extending the loop to size d results in an extension free energy

$$\varepsilon_{\text{ext}} \approx k_B T d^2/s^2 \approx k_B T\,(m-1)\,d^2/(nl^2) \quad (18)$$

per loop. At equilibrium, the extension free energy ε_{ext} of one loop is balanced by the energetic gain $f_{\text{gain}} \approx \delta k_B T$ from one adsorption. From $\varepsilon_{\text{ext}} \approx f_{\text{gain}}$, we get the equilibrium number of adsorbed sticky monomers

$$m \approx 1 + n\delta l^2/d^2 \quad (19)$$

where eq 18 for ε_{ext} was used. At $l/d = n^{-1/2}\delta^{-1/2}$, the smallest number of adsorbed sticky monomers $m = 2$ corresponds to the adsorption of two sticky end monomers with the whole chain in a single loop conformation. With increasing l/d, in regime II as illustrated in Figure 4, the equilibrium number of adsorbed sticky monomers increases until it reaches the maximum value $m = n + 1$ at $l/d = \delta^{-1/2}$. This increase in the number of adsorbed sticky monomers with the ratio l/d in regime II is shown in Figure 5a.

Finally, in regime III with $\delta^{-1/2} < l/d < 1$, the equilibrium number of adsorbed sticky monomers saturates at its maximum value $m = n + 1$ (Figure 5a), corresponding to the adsorption of all the sticky monomers of the chain. The extension factor d/l of the linking

segments of q monomers between two neighboring adsorbed sticky monomers decreases from $\delta^{1/2}$ at the boundary between regimes II and III to unity for unstretched linking segments at the boundary between regimes III and IV.

In regimes II and III, the conformation of a stretched loop along the adsorption surface is a one-dimensional array of tension blobs.[32] The number of tension blobs per stretched loop is

$$p_t \approx \varepsilon_{ext}/k_B T \quad (20)$$

since the extension free energy per tension blob is on the order of $k_B T$, and the tension blob size is

$$\xi_t \approx d/p_t \quad (21)$$

In regime II, the number of tension blobs per stretched loop $p_t \approx \delta$ as the extension free energy of the stretched loop $\varepsilon_{ext} \approx f_{gain} \approx \delta k_B T$. Accordingly, the tension blob size $\xi_t \approx d/\delta$. This size ξ_t decreases from $n^{1/2}\delta^{-1/2}l$ at $l/d = n^{-1/2}\delta^{-1/2}$ to $\delta^{-1/2}l$ at $l/d = \delta^{-1/2}$. In regime III, the extension free energy of the stretched loop formed by a linking segment is $\varepsilon_{ext} \approx k_B T d^2/l^2$. As a result, the number of tension blobs $p_t \approx d^2/l^2$ decreases from δ at $l/d = \delta^{-1/2}$ to unity at $l/d = 1$ with no stretching of loops, while the tension blob size $\xi_t \approx l/d^2$ increases from $\delta^{-1/2}l$ to l.

An adsorbed chain in regimes II and III is effectively in a quasi-two-dimensional (quasi-2d) conformation along the adsorption surface with stretched loops as effective monomers of size $b_{eff} \approx d$. Since an adsorption site cannot be simultaneously occupied by two sticky monomers, adsorbed sticky monomers that occupy adsorption sites repel each other with excluded area on the order of d^2, which is equal to the area ${b_{eff}}^2$ of effective monomers. As a result, the conformation of the quasi-2d polymer along the adsorption surface can be described as a two-dimensional (2-d) self-avoiding random walk of effective monomers, and the chain size $R_\parallel$ along the adsorption surface is

$$R_\parallel \approx (m-1)^{3/4} b_{eff} \approx (m-1)^{3/4} d \quad (22)$$

Substituting eq 19 for the number of adsorbed sticky monomers m per chain in regime II and $m = n + 1$ for regime III into eq 22, we obtain that

$$R_\parallel \approx \begin{cases} n^{3/4}\delta^{3/4}(l/d)^{1/2}l, & \text{regime II}(n^{-1/2}\delta^{-1/2} < l/d < \delta^{-1/2}) \\ n^{3/4}(l/d)^{-1}l, & \text{regime III}(\delta^{-1/2} < l/d < 1) \end{cases} \quad (23)$$

As shown in Figure 5b, the size of an adsorbed multisticker polymer along the adsorption surface increases with the ratio l/d in regime II as $R_\parallel/l \sim (l/d)^{1/2}$ from $R_\parallel \approx n^{1/2}\delta^{1/2}l$ at $l/d = n^{-1/2}\delta^{-1/2}$ to the stretched size $R_\parallel \approx n^{3/4}\delta^{1/2}l$ at $l/d = \delta^{-1/2}$. In contrast, the size $R_\parallel$ increases with d as $R_\parallel \approx n^{3/4}d$ or decreases with l/d as $R_\parallel/l \sim (l/d)^{-1}$ in regime III before reaching the size $n^{3/4}l$ of a 2-d self-avoiding random walk of n unperturbed linking segments at $l/d = 1$.

For an adsorbed multisticker polymer in regimes II and III, the size $R_\perp$ of the stretched loop normal to the adsorption surface and hence the height of the adsorbed polymer are almost identical to the unperturbed size of a stretched loop. In regime II

$$R_\perp \approx s \approx \left(\frac{n}{m-1}\right)^{1/2} l \approx \delta^{-1/2} d \quad (24)$$

where eq 19 was used for m. As shown in Figure 5c, the size $R_\perp$ in regime II decreases from the ideal chain size $n^{1/2}l$ at $l/d = n^{-1/2}\delta^{-1/2}$ down to the unperturbed size l of a linking segment at $l/d = \delta^{-1/2}$. In regime III where each stretched loop consists of only one linking segment, the size $R_\perp$ remains at the unperturbed size l of a linking segment.

3.1.3. Regime IV: Random Walk of Unstretched Loops—At a surface with densely distributed adsorption sites (regime IV with $l/d > 1$ in Figure 4), all sticky monomers along the chain are adsorbed. However, unlike in regime III, the polymer does not have to stretch to achieve this, and thus all linking segments are almost unperturbed. The whole chain can be described as a quasi-2d polymer with linking segments as effective monomers of size $b_{\text{eff}} \approx l$. As in regimes II and III, the one-to-one binding between a sticky monomer and an adsorption site leads to exclusion between effective monomers. Since the average distance d between adsorption sites is smaller than the size l of effective monomers, the excluded area $\sim d^2$ associated with an effective monomer is smaller than the effective monomer area $\sim l^2$, resulting in partial overlap between effective monomers. With increasing ratio l/d, the repulsion between effective monomers due to the excluded area $\sim d^2$ decreases and eventually becomes weaker than the three-body repulsion between monomers in a theta solvent. Therefore, the dominant repulsion energy in an adsorbed multisticker polymer changes with increasing l/d from the one due to two-body excluded area interactions between effective monomers to the three-body repulsion energy.

The repulsion energy due to two-body interactions with the excluded area $\approx d^2$ per effective monomer is

$$f_{2-\text{body}} \approx k_{\text{B}}T\frac{d^2n^2}{{R_\parallel}^2} \quad (25)$$

in which $R_\parallel$ is the size of the adsorbed polymer along the adsorption surface. The three-body repulsion energy is related to the three-body interaction coefficient $w \approx b^6$ and the pervaded volume $V \approx R_\parallel^2 R_\perp$ of the adsorbed polymer as

$$f_{3-\text{body}} \approx k_{\text{B}}Tw\frac{(nq)^3}{V^2} \approx k_{\text{B}}T\frac{n^3l^4}{{R_\parallel}^4} \quad (26)$$

where we used $R_\perp \approx l$ for the chain size normal to the adsorption surface in regime IV. In addition, the extension free energy of a polymer stretched relative to the ideal random walk conformation with chain size $\approx n^{1/2}l$ is

$$f_{\text{ext}} \approx k_{\text{B}}T\frac{{R_{\|}}^2}{nl^2} \quad (27)$$

As a result, the overall free energy of an adsorbed multisticker polymer

$$f \approx f_{2-\text{body}}+f_{3-\text{body}}+f_{\text{ext}} \approx K_{\text{B}}T\left(\frac{d^2n^2}{{R_{\|}}^2}+\frac{n^3l^4}{{R_{\|}}^4}+\frac{{R_{\|}}^2}{nl^2}\right) \quad (28)$$

The balance between the dominant repulsion energy, either $f_{2\text{-body}}$ or $f_{3\text{-body}}$, and the entropic extension energy f_{ext} minimizes the overall free energy f and therefore determines the equilibrium chain size $R_{\|}$ along the adsorption surface. Using eqs 25–27, one obtains

$$R_{\|} \approx \begin{cases} n^{3/4}(l/d)^{-1/2}l, & 1<l/d<n^{1/6}(f_{\text{ext}} \approx f_{2-\text{body}}>f_{3-\text{body}}) \\ n^{2/3}l, & l/d>n^{1/6}(f_{\text{ext}} \approx f_{3-\text{body}}>f_{2-\text{body}}) \end{cases} \quad (29)$$

As shown in Figure 5b, the size of an adsorbed multisticker polymer along the adsorption surface in regime IV decreases as $R_{\|}/l \sim (l/d)^{-1/2}$ at $1 < l/d < n^{1/6}$ because of decreasing excluded area of effective monomers, whereas remains at $R_{\|} \approx n^{2/3}l$ at $l/d > n^{1/6}$ due to a constant three-body repulsion energy. Note that throughout regimes II and III we ignore the three-body repulsion energy between monomers as the repulsion energy of the adsorbed polymer is dominated by the two-body excluded area repulsion between adsorbed sticky monomers.

3.2. Multichain Adsorption of Multisticker Polymers

We study the adsorption of multiple multisticker polymers from a bulk solution with polymer volume fraction φ_{bulk} at different values of the parameter l/d. For exponentially low bulk volume fraction $\varphi_{\text{bulk}} < e^{-m\delta}$ (see Figure 5a for the l/d-dependent value of the average number m of adsorbed stickers per chain), the adsorption surface is partially covered because of the high translation entropy cost to bring polymers to the surface. Therefore, polymers adsorbed from exponentially dilute solutions do not overlap with each other and adopt essentially the same conformations as in single multisticker polymer adsorption. There are four different regimes, regimes I–IV in Figure 6, corresponding respectively to regimes I–IV in Figure 4 for single multisticker polymer adsorption.

In contrast, the translational entropy loss of polymers adsorbed from solutions with high bulk volume fraction φ_{bulk} is small compared to other terms of the free energy change upon adsorption and thus can be ignored. The equilibrium structure of chains adsorbed from solutions with relatively high volume fraction depends on the ratio l/d. We identify four different multichain adsorption regimes shown as regimes V–VIII in Figure 6.

3.2.1. Regime V: Mushroom Meadow—In regime V with $l/d < n^{-1/2}$, adsorption sites on the surface are widely separated with the average distance d between neighboring sites larger than the unperturbed size $n^{1/2}l$ of the polymers. As illustrated in Figure 6, the adsorbed polymers adopt the mushroom conformations with each chain occupying one adsorption site, and the entire adsorption layer resembles a mushroom meadow. Because of

the weaker proximity effects near chain ends, most chains are grafted to the adsorption sites via one of their sticky end monomers. Almost all adsorption sites are occupied without overlap of adsorbed chains. Note that the height H of the adsorption layer in this regime is on the order of the ideal chain size $n^{1/2}l$.

Regimes in the low φ_{bulk} limit that cross over to regime V as the bulk volume fraction φ_{bulk} increases include regime I and the part of regime II with $n^{-1/2}\delta^{-1/2} < l/d < n^{-1/2}$. Here we assume that $n > \delta \gg 1$ and $n^{-1/2}$ lies between $n^{-1/2}\delta^{-1/2}$ and $\delta^{-1/2}$, the two boundaries of regime II. (If instead $\delta > n \gg 1$, regime I, the entire regime II, and the part of regime III with $\delta^{-1/2} < l/d < n^{-1/2}$ cross over to regime V as the bulk volume fraction φ_{bulk} increases.) The crossover from regime I to regime V occurs at the bulk volume fraction $\varphi_{bulk} \approx e^{-\delta}$, where according to eq 6 mushrooms cover about half of the adsorption sites ($\theta \approx 1/2$) with the adsorption energy per mushroom $\varepsilon_{ads} \approx -\delta k_B T$.

For the part of regime II with $n^{-1/2}\delta^{-1/2} < l/d < n^{-1/2}$, the crossover to regime V with increasing bulk volume fraction φ_{bulk} starts with the overlap of adsorbed polymers in the conformations of a 2-d self-avoiding random walk of m stretched loops. At the overlap of adsorbed chains in a 2-d self-avoiding random-walk conformation, the fraction of occupied adsorption sites $\theta^{overlap} \approx m^{-1/2} < 1$ as calculated in section C of the Supporting Information, and the corresponding bulk volume fraction $\phi_{bulk}^{overlap} \approx \theta^{overlap} e^{-m\delta} \approx m^{-1/2} e^{-m\delta}$. As bulk volume fraction increases above $\phi_{bulk}^{overlap}$, a higher fraction of adsorption sites are occupied ($\theta > \theta^{overlap}$), and the adsorbed polymers adopt conformations deswollen with respect to 2-d self-avoiding random-walk conformation. As estimated in section C of the Supporting Information, at bulk volume fraction $\phi_{bulk}^{full} \approx e^{-m\delta}$, almost all adsorption sites are occupied ($\theta \approx 1$), and adsorbed polymers form a quasi-2d melt with stretched loops of size d as effective monomers. Chains are essentially segregated from each other in the quasi-2d melt, and their size along the surface $R_{||} \approx m^{1/2}d$.[34,35] At bulk volume fraction higher than ϕ_{bulk}^{full}, the average number of adsorption sites occupied by an adsorbed chain decreases so that more chains can be adsorbed at almost full occupation of adsorption sites. As shown in section C of the Supporting Information, at bulk volume fraction $\varphi_{bulk} \approx e^{-2\delta}$ each adsorbed chain occupies only two neighboring adsorption sites, adopting the conformation of a single stretched loop. With further increasing bulk volume fraction, a single stretched loop can be replaced by two mushrooms; hence, the adsorption layer transforms from a monolayer of stretched loops to a mixture of stretched loops and mushrooms and eventually to a mushroom meadow. The entire crossover to regime V ends at $\varphi_{bulk} \approx e^{-\delta}$ as indicated in Figure 6.

3.2.2. Regime VI: Self-Similar Carpet—In regime VI with $n^{-1/2} < l/d < 1$, a polymer can occupy multiple adsorption sites without stretching. The structure of the adsorption layer formed by overlapping polymers is similar to the self-similar carpet formed by weakly adsorbed polymers.[5,7] The correlation length ξ in this carpet scales linearly with the distance z from the adsorption surface. Since the smallest loop connecting neighboring adsorption sites is of size d, the smallest correlation length ξ is set by the size d of this smallest loop. The upper limit of ξ away from the adsorption surface is the unperturbed chain size $n^{1/2}l$.

The monomer volume fraction profile in a theta solvent decreases with the distance z from the surface as

$$\phi(z) \approx b/\xi(z) \approx b/z, \quad \text{for } d < z < n^{1/2}l \quad (30)$$

The height of the adsorption layer is $H \approx n^{1/2}l$, with the outer part of the adsorption layer determining the layer thickness.

The part of regime II with $n^{-1/2} < l/d < \delta^{-1/2}$ and regime III cross over to regime VI with increasing bulk volume fraction φ_{bulk}. (Note that if $\delta > n \gg 1$, only the part of regime III with $n^{-1/2} < l/d < 1$ crosses over to regime VI.) Similar to the crossover from the part of regime II with $n^{-1/2}\delta^{-1/2} < l/d < n^{-1/2}$ to regime V, as bulk volume fraction φ_{bulk} increases, adsorbed chains in the conformation of a 2-d self-avoiding random walk of stretched loops first overlap with each other at $\phi_{\text{bulk}}^{\text{overlap}} \approx m^{-1/2}\mathrm{e}^{-m\delta}$ and then transform to a dense quasi-2d melt at $\varphi_{\text{bulk}} \approx \mathrm{e}^{-m\delta}$, consisting of essentially segregated chains that occupy almost all adsorption sites. At higher bulk volume fraction $\varphi_{\text{bulk}} > \mathrm{e}^{-m\delta}$, more chains are adsorbed onto the surface, and an adsorbed chain is on average bound to fewer adsorption sites. Accordingly, the loops connecting neighboring adsorption sites become less stretched. As calculated in section D of the Supporting Information, at bulk volume fraction $\phi_{\text{bulk}}^{\text{unstretched}} \approx \mathrm{e}^{-n\delta l^2/d^2}$ (see the blue dash-dotted line in Figure 6), the loops connecting neighboring adsorption sites adopt unstretched conformations. As bulk volume fraction φ_{bulk} increases further, the conformation of an adsorbed chain transforms from a quasi-2d random walk of unstretched loops of uniform size on the order of d to that consisting of loops and tails of varying sizes as in a self-similar carpet. The calculation in section D of the Supporting Information shows that at bulk volume fraction $\phi_{\text{bulk}}^{\text{carpet}} \approx \mathrm{e}^{-n\delta(l/d)^2/\ln(n^{1/2}l/d)}$, a self-similar carpet is fully developed, and the crossover to regime VI is complete. Details about the conformational changes of the adsorbed chains and the increase of the adsorbed amount of polymers with bulk volume fraction φ_{bulk} during the crossover to regime VI are presented in section D of the Supporting Information.

3.2.3. Regimes VII and VIII: Brush of Loops Covered by Self-Similar Carpet—

Consider the multichain adsorption regimes for multisticker polymers with $l/d > 1$ at relatively high bulk volume fraction. Since the average spacing d between adsorption sites is smaller than the average distance l between sticky monomers, adsorbed chains strongly overlap with each other to occupy the adsorption sites densely covering the surface, forming a brush layer close to the adsorption surface.[36] The height of the brush H^{brush} is determined by the size of a linking segment containing q monomers, which is the smallest loop between surface adsorption sites. Similar to the brush layer formed by telechelic polymers (regimes VI and VII in Figure 2), the correlation length in the brush of loops

$$\xi^{\text{brush}} \approx \begin{cases} d, & \text{regime VII}(1 < l/d < \delta^{1/2}) \\ l/\delta^{1/2}, & \text{regime VIII}(l/d > \delta^{1/2}) \end{cases} \quad (31)$$

and the height of the brush

$$H^{\mathrm{brush}} \approx \begin{cases} l^2/d, & \text{regime VII}(1<l/d<\delta^{1/2}) \\ l\delta^{1/2}, & \text{regime VIII}(l/d>\delta^{1/2}) \end{cases} \quad (32)$$

A polymer chain can be fully embedded in the brush with a succession of extended linking segments along the chain, each connecting two adsorption sites separated by a distance on the order of the ideal size l of linking segments, as illustrated in Figure 7a. In this way, all the $n + 1$ sticky monomers along the chain can be adsorbed to the surface. However, a single chain in this conformation can unfold some of the extended linking segments and release the associated adsorption sites. As a result, an adsorbed polymer connects adsorption sites via loops of various sizes. The released adsorption sites can be occupied by other adsorbed chains with no change of the adsorption energy of the whole layer. However, allowing the variation of loop size lowers the entropic part of the free energy of the adsorption layer, making an adsorption layer consisting of loops of various sizes thermodynamically more favorable than an adsorption layer in which all loops are extended linking segments.

Among the loops of various sizes on the adsorption surface, the smallest loops formed by linking segments are entirely located in the brush layer. Orange loops in Figure 7a illustrate some of these smallest loops. In contrast, only the portions near the ends of a larger loop dwell in the brush, while the rest of the loop is located above the brush. For polymers above the brush, the correlation length ξ linearly increases with the distance $z - H^{\mathrm{brush}}$ from value l at the top edge of the brush layer until it reaches the chain size $n^{1/2}l$, as shown in Figure 7b. Thus, polymers above the brush form a self-similar carpet analogous to the carpet in regime VI. Consequently, as depicted in Figure 7a, the adsorbed multisticker polymers in regimes VII and VIII possess a two-layer structure including the brush layer and the self-similar carpet on the top of it.

The self-similar carpets are similar for regimes VII and VIII with no dependence on the brush below. Recall that in the second layer for telechelic polymers in regimes VI and VII (Figure 2) tails of open chains weakly overlap. In light of this, at distance $z^{\mathrm{carpet}} \approx z - H^{\mathrm{brush}} \approx l$ above the top edge of the brush layer, the correlation length ξ^{carpet} is on the order of the unperturbed size l of linking segments. As shown in Figure 7b, across the brush–carpet boundary $z \approx H^{\mathrm{brush}}$, the correlation length of polymers increases to reduce the interaction energy of overlapping chain sections. At $z^{\mathrm{carpet}} \approx n^{1/2}l$, ξ^{carpet} increases to the unperturbed size $n^{1/2}l$ of polymers in the dilute bulk solution. Thus, the height of the carpet layer is on the order of the unperturbed chain size

$$H^{\mathrm{carpet}} \approx n^{1/2}l \quad (33)$$

Note that for $n > \delta \gg 1$, the carpet is thicker than the brush in both regime VII and regime VIII, since $H^{\mathrm{carpet}} \approx n^{1/2}l > \delta^{1/2}l \geq H^{\mathrm{brush}}$ (see eq 32 for H^{brush}). Therefore, the thickness $H \approx H^{\mathrm{brush}} + H^{\mathrm{carpet}}$ of all adsorbed polymers is determined by the height of carpet. However, for $\delta > n \gg 1$, the carpet is thicker than the brush ($H^{\mathrm{carpet}} > H^{\mathrm{brush}} \approx l^2/d$) only in the part of regime VII with $1 < l/d < n^{1/2} < \delta^{1/2}$, whereas the brush is thicker than the carpet in the part of regime VII with $n^{1/2} < l/d < \delta^{1/2}$ and the entire regime VIII.

The brush-under-carpet state in regime VIII contains a brush of extended loops with both the correlation length ξ^{brush} (eq 31) and the brush height H^{brush} (eq 32) controlled by the adsorption strength δ and independent of the ratio l/d. Adsorption in this regime is similar to nonselective adsorption of multisticker polymers in which any place at the adsorption surface can strongly (i.e., with an adsorption energy $\delta k_B T \gg k_B T$) yet reversibly adsorb a sticker, corresponding to the large l/d limit in our selective adsorption model. Thus, one can apply our brush-under-carpet model at the saturation of the brush layer to describe the adsorbed multisticker polymers in nonselective strong adsorption.

Our scaling description of strongly and selectively adsorbed multisticker polymers at $l/d > 1$ as a polymer brush capped by a self-similar carpet is similar to the one proposed by Marques and Joanny[25] for the multichain adsorption of copolymers where one type of monomers regularly distributed along the chain acts as stickers that bind strongly to the adsorption surface. Using our notation, we describe below the scaling model Marques and Joanny constructed for the layer of adsorbed copolymers, which are equivalent to the multisticker polymers in this paper. Marques and Joanny's model consists of a cascade of brushes at the adsorption surface and covered by a self-similar carpet. Close to the adsorption surface, extended chain segments each containing $\approx q/2 \approx q$ monomers form the first brush, in which the number of extended segments per unit area is σ_1 and the correlation blob size $\xi_1 \approx \sigma_1^{-1/2}$. Part of the extended segments in the first brush belong to looped linking segments with both end sticky monomers adsorbed, whereas the rest of the extended segments in the first brush, the fraction of which is k, are connected to chain segments above the first brush. The second brush on top of the first one also consists of extended segments containing $\approx q$ monomers. However, the number of extended segments per unit area is reduced to $\sigma_2 \approx \sigma_1 k$, as only a fraction k of the extended segments in the first brush do not loop back to the adsorption surface. Therefore, the correlation blob size in the second brush increases to $\xi_2 \approx \xi_1 k^{-1/2}$. Through open extended segments that do not loop back to the bottom of a brush layer, a series of brushes are built recursively until the correlation blob size in the jth layer $\xi_j \approx \xi k^{-(j-1)/2}$ becomes on the order of the unperturbed size l of linking segments, the smallest correlation blob size in the self-similar carpet.

Both Marques and Joanny's model and our model contain a brush formed by extended segments each consisting of $\approx q$ monomers at the adsorption surface and a self-similar carpet. The two models differ in the way they connect the brush attached to the adsorption surface to the carpet. While Marques and Joanny introduced a cascade of intermediate brushes to gradually increase the correlation length from $\xi_1 \ll l$ to the order of l, the smallest blob size in the self-similar carpet, we directly connect the brush at the adsorption surface to the carpet. For a cascade of j_{max} brushes, our calculation in section G of the Supporting Information shows that the interaction free energy associated with the part of the cascade between the first brush and the carpet is $\tilde{f}_{j_{max}-2} \approx k_B T p_1^{-2/(j_{max}-1)+1}$ per extended segment in the first brush where the number of correlation blobs per segment is $p_1 \gg 1$. For directly connected brush and carpet, the free energy penalty associated with the large gradient of polymer concentration in the crossover region between the brush and carpet is about $\tilde{f}_{crossover} \approx k_B T$ per extended segment in the brush as estimated in section G of the Supporting Information. Comparing $\tilde{f}_{j_{max}-2}$ and $\tilde{f}_{crossover}$, we find that Marques and

Joanny's model with one or more intermediate brushes is thermodynamically less favorable than our model as $\tilde{f}_{j_{\max}-2} > \tilde{f}_{\text{crossover}}$ for a cascade with $j_{\max} \geq 3$. Their model with $j_{\max} = 2$ is essentially our model with directly connected brush and carpet. More detailed comparison of the two models is provided in section G of the Supporting Information.

The increase of the thickness H of adsorbed polymers as a function of the ratio l/d at relatively high bulk volume fraction $\varphi_{\text{bulk}} > e^{-\delta}$ is shown in Figure 8. In regime V where each adsorbed chain adopts the mushroom conformation and regime VI where the adsorption layer is a self-similar carpet, the thickness H is on the order of the unperturbed chain size $n^{1/2}l$. As a brush layer forms underneath the carpet with increasing l/d in regime VII, the thickness of the brush layer H^{brush} increases as $\tilde{l}^2/d$ (eq 32), and therefore the thickness of the entire adsorption layer $H \approx H^{\text{brush}} + H^{\text{carpet}}$ increases as $\sim \tilde{l}^2/d$. Finally, in regime VIII, the thickness saturates at $H \approx H^{\text{brush}} + H^{\text{carpet}} \approx \delta^{1/2}l + n^{1/2}l$ determined by the adsorption strength δ and the number n of sticky monomers per chain, which control the brush height H^{brush} and the carpet height H^{carpet}, respectively.

Regime IV in the low φ_{bulk} limit crosses over to regime VII or VIII as the bulk volume fraction φ_{bulk} increases. Similar to the crossover to regime V or VI, the crossover to regime VII or VIII begins with the overlap of adsorbed chains. The entire surface can be divided into adsorption regions with dimensions on the order of the unperturbed size l of linking segments. Each adsorption region can be either occupied by one unstretched loop formed by one linking segment or not occupied at all. At the overlap of adsorbed chains, the fraction of occupied adsorption regions can be estimated as

$$\eta \approx \eta^{\text{overlap}} \approx n/(R_{\parallel}{}^2/l^2) \approx \begin{cases} n^{-1/2}(l/d), & 1<l/d<n^{1/6} \\ n^{-1/3}, & l/d>n^{1/6} \end{cases} \quad (34)$$

where eq 29 for the chain size $R_{/\!/}$ in regime IV was used. As calculated in section E of the Supporting Information, the overlap of adsorbed chains with $\eta \approx \eta^{\text{overlap}}$ occurs at bulk volume fraction $\phi_{\text{bulk}}^{\text{overlap}} \approx \eta^{\text{overlap}} e^{-n\delta}$. At higher bulk volume fraction $\varphi_{\text{bulk}} \approx e^{-n\delta}$, adsorbed chains form a dense quasi-2d melt, while almost the entire surface is covered by unstretched loops, i.e., the fraction of occupied adsorption regions $\eta \approx 1$. Subsequently, as the bulk volume fraction φ_{bulk} further increases, a self-similar carpet first forms at the adsorption surface and then a brush layer builds underneath the carpet. In section E of the Supporting Information, we show that the carpet layer is fully developed at the bulk volume fraction $\phi_{\text{bulk}}^{\text{carpet}} \approx e^{-n\delta/\ln n^{1/2}}$ independent of the ratio l/d (as indicated by the green dashed line in Figure 6), while the development of the brush layer is completed at $\phi_{\text{bulk}} \approx e^{-n\delta\xi_{\text{brush}}{}^2/l^2}$, which is $e^{-n\delta d^2/l^2}$ and e^{-n} for the crossover to regimes VII and VIII, respectively. A detailed description of the formation of the two-layer structure of the adsorbed polymers with increasing bulk volume fraction φ_{bulk} is given in section E of the Supporting Information.

3.3. Adsorbed Amount of Multisticker Polymers

The adsorbed amount Γ of multisticker polymers is determined as the number of monomers in adsorbed chains per unit area of the adsorption surface. The adsorbed chains are defined as polymers with at least one sticky monomer adsorbed. In sections C–E of the Supporting Information describing the crossovers from adsorption regimes at low φ_{bulk} to respective regimes at high φ_{bulk}, we show the increase of the adsorbed amount Γ with the bulk volume fraction φ_{bulk} during each crossover. Below we focus on the adsorption regimes at relatively high polymer volume fraction ($\varphi_{bulk} > e^{-\delta}$ if $n > \delta$ and $\varphi_{bulk} > e^{-n}$ if $n < \delta$). The scaling of the adsorbed amount Γ with l/d in different high-φ_{bulk} regimes is shown schematically in Figure 9.

In regime V, there is one polymer per adsorption site, resulting in the adsorbed amount $\Gamma \approx nq/d^2$. Since the surface density of adsorption sites is $\Sigma \approx 1/d^2$, this result indicates that for polymers adsorbed as mushrooms the adsorbed amount Γ scales linearly with the surface density Σ. In regime VI, the adsorbed amount Γ can be obtained from the monomer volume fraction profile $\varphi(z) \approx b/z$ (eq 30) in the self-similar carpet

$$\begin{aligned}\Gamma \approx \Gamma^{\text{carpet}} &\approx \int_d^{n^{1/2}l} b^{-3}\phi(z)dz \approx b^{-2}\int_d^{n^{1/2}l} z^{-1}dz \\ &\approx b^{-2}\ln(n^{1/2}l/d) \sim \ln \sum\end{aligned} \quad (35)$$

In this regime, the adsorbed amount increases logarithmically with the surface density as $\Gamma \sim \ln \Sigma$, which is much slower than the increase in regime V. However, as shown in Table 5 in section F of the Supporting Information, the adsorbed amount for the self-similar carpet in regime VI scales as

$$\Gamma^{\text{carpet}} \sim d^{1/\nu-2} \sim \sum^{1-1/(2\nu)} \sim \sum^{0.15} \quad (36)$$

in an athermal solvent with $\nu \approx 0.588$.

In regimes VII and VIII, the adsorbed amount Γ has separate contributions from the brush and the self-similar carpet, $\Gamma \approx \Gamma^{\text{brush}} + \Gamma^{\text{carpet}}$. In the brush layer with the correlation length ξ^{brush}, there are $\approx q/2 \approx q$ monomers per surface area $\approx (\xi^{\text{brush}})^2$, so the brush contributes $\Gamma^{\text{brush}} \approx q/(\xi^{\text{brush}})^2$ to the adsorbed amount. In regime VII, $\xi^{\text{brush}} \approx d$ and $\Gamma^{\text{brush}} \approx q/d^2$, whereas in regime VIII, $\xi^{\text{brush}} \approx l/\delta^{1/2}$ and $\Gamma^{\text{brush}} \approx \delta/b^2$ saturates at a value determined by the adsorption strength δ. For the carpet in both regimes, using the monomer volume fraction profile

$$\phi\left(z^{\text{carpet}}\right) \approx b/\xi\left(z^{\text{carpet}}\right) \approx b/z^{\text{carpet}} \quad (37)$$

we calculate the contribution to the adsorbed amount from the carpet

$$\begin{aligned}\Gamma^{\text{carpet}} &\approx \int_l^{n^{1/2}l} b^{-3}\phi\left(z^{\text{carpet}}\right) dz^{\text{carpet}} \\ &\approx b^{-2}\int_l^{n^{1/2}l} \left(1/z^{\text{carpet}}\right) dz^{\text{carpet}} \\ &\approx b^{-2}\ln\left(n^{1/2}\right) \approx b^{-2}\ln n\end{aligned} \quad (38)$$

which is independent of the surface density Σ of adsorption sites. As a result, the adsorbed amount in the entire adsorption layer is

$$\Gamma \approx \Gamma^{\mathrm{brush}} + \Gamma^{\mathrm{carpet}} \approx \begin{cases} \frac{q}{d^2} + \frac{\ln n}{b^2} \approx \frac{q}{d^2} \sim \sum, & \text{regime VII} (1 < l/d < \delta^{1/2}) \\ \frac{\delta}{b^2} + \frac{\ln n}{b^2} \approx \frac{\delta}{b^2}, & \text{regime VIII} (l/d > \delta^{1/2}) \end{cases} \quad (39)$$

In regime VII, $\Gamma \sim \Sigma$ indicates the recovery of the linear increase of the adsorbed amount with the surface density of adsorption sites. Furthermore, since $\Gamma^{\mathrm{brush}} \gg \Gamma^{\mathrm{carpet}}$, the dominant contribution to Γ comes from the brush in regimes VII and VIII.

4. SUMMARY

We have developed a scaling theory for strong selective adsorption of polymers containing sticky monomers onto a surface with uniformly distributed adsorption sites. Selectivity in our adsorption model originates from the fact that sticky monomers can be strongly bound to the adsorption sites on the surface while other monomers do not specifically bind to the adsorption sites. One distinctive feature of selective adsorption is its dependence on the ratio l/d of the mean-square distance l between neighboring sticky monomers along the unperturbed chain and the average spacing d between neighboring adsorption sites on the surface. The competition between the entropic penalty associated with the deformation of chains, which depends on the ratio l/d, and the energetic gain $\delta k_{\mathrm{B}} T$ from binding to an adsorption site determines the optimized structure of adsorbed polymers. We have studied the strong selective adsorption of telechelic and multisticker polymers. Different single-chain adsorption regimes have been identified for both types of polymers (as shown in Figures 1 and 4). The multichain adsorption of polymers depends on the volume fraction φ_{bulk} of polymers in the bulk solution in addition to the ratio l/d. We have constructed diagrams illustrating different adsorption regimes as a function of l/d and φ_{bulk} for telechelic (Figure 2) and multisticker polymers (Figure 6). For each regime, the conformations of adsorbed chains have been determined, and both the thickness H of the adsorption layer and the adsorbed amount Γ of polymers in the layer have been calculated. Our results for $l/d > \delta^{1/2}$ can be applied to nonselective strong adsorption in which a sticky monomer along the chain can be reversibly bound to anywhere on the adsorption surface with the binding energy $\gg k_{\mathrm{B}} T$.

Experimentally, the adsorption layer is typically quantified by the adsorbed amount of polymer mass per unit area. Crespo-Biel et al.[21] studied the selective adsorption of poly(isobutene-*alt*-maleic acid)s modified with hydrophobic groups (*p*-tetrabutylphenyl or adamantly groups) onto a β-cyclodextrin self-assembled monolayer (β-CD SAM) through the inclusions of the hydrophobic groups into the cavities of β-CDs. On the basis of AFM scratching experiment in air, they estimated that the dry thickness of the adsorption layer is $\approx$ 0.5 nm independent of the polymer volume fraction in the explored range. The measured thickness essentially reflects the adsorbed amount of polymers, as the fluffy adsorption layer with dangling tails in the solution collapses in air to a dense thin layer covering the substrate. The observed thickness $\approx$ 0.5 nm is on the order of the monomer size and therefore indicates that there is roughly one monomer within the surface area equal to the

square of the monomer size, i.e., $\Gamma \approx 1/b^2$ using the notation of our scaling theory. The average contour length $l_{contour}$ between hydrophobic groups (1.6–5.4 nm) matches the average distance d between β-CD cavities (ca. 2 nm). This scenario is similar to the multichain adsorption of multisticker polymers with the ratio $l/d \approx 1$. Our scaling theory predicts that at $l/d \approx 1$ the adsorption layer at relatively high volume fraction of polymers in the bulk solution can be represented as a self-similar carpet and the adsorbed amount $\Gamma \approx \ln n/b^2 \approx 1/b^2$ (Figure 9). The predicted adsorbed amount agrees with the implication of the thickness of the dry adsorption layer in Crespo-Biel et al.'s experiment.

In a recent experiment, Dubacheva et al.[24] investigated selective adsorption of hyaluronic acids modified with host β-cyclodextrin (HA-β-CD) onto self-assembled monolayers functionalized with guest ferrocene (SAM-Fc) based on the host/guest binding of β-CD/Fc pairs. They measured the dependence of the adsorbed amount Γ of HA-β-CDs per unit surface area on the ferrocene surface density Σ and observed that the adsorbed amount Γ increases superlinearly with increasing surface density Σ before saturating at sufficiently high Σ. The average contour distance between β-CDs along the polymer chain is $l_{contour}$ = 33 nm, and the estimated root-mean-square spacing between neighboring β-CDs is $l \approx 6.2$ nm. The superlinear rise and subsequent saturation of the adsorbed amount Γ occur when the average distance between ferrocenes on the surface d = 1.3–2.5 nm, corresponding to the ratio $l/d > 1$. In our scaling theory, we predict that at $l/d > 1$ there is a linear increase of Γ with the surface density Σ followed by a saturation of Γ at a value controlled by the adsorption strength. Our prediction qualitatively agrees with the experimental result by Dubacheva et al. However, the superlinear increase of Γ with Σ cannot be explained based on our theory. A recent self-consistent field theory calculation[37] suggests that the super-linear rise of Γ with Σ could be related to the crossover adsorption regime between well-defined scaling regimes.

In our analysis of strong selective adsorption, we assume that sticky monomers are regularly distributed along the polymer chain; i.e., the monomer number q in a linking segment between two neighboring sticky monomers is almost constant. However, variation in q is almost inevitable in synthetic polymers. Below we briefly discuss the effects of the polydispersity in q on strong selective adsorption of telechelic polymers (see Figure 2). Regimes affected by the polydispersity in q include regimes II and IV where an adsorbed polymer is stretched to form a loop connecting two neighboring adsorption sites and regimes VI and VII where a brush of extended loops form at the adsorption surface. The extension free energy of an adsorbed chain as a stretched loop in regimes II and IV decreases with q, favoring the adsorption of longer chains. In contrast, the interaction free energy of an adsorbed chain in the brush of extended loops in regimes VI and VII increases with q, and the adsorption of shorter chains is preferred. In both cases, the preferential adsorption of chains with q deviating from the most probable value $\langle q \rangle$ is possible for relatively polydisperse samples with smaller entropic free energy loss due to the adsorption of these "atypical" chains. As demonstrated in section H of the Supporting Information, the preferential adsorption of such atypical chains is expected if the polydispersity index is larger than $1 + (\langle l \rangle/d)^4$ in regimes II and IV and larger than $1 + (\langle l \rangle/d)^{-4}$ in regime VI and $1 + \delta^{-2}$ in regime VII for both a Gaussian distribution and a Poisson distribution of q around the most probable value $\langle q \rangle \approx \langle l \rangle^2/b^2$.

Our discussion of the polydispersity in the monomer number q per linking segment is based on the adsorption of telechelic polymers but can be generalized to the adsorption of multisticker polymers. Similar to our examination of the polydispersity in q, the effects of the polydispersity in the spacing d between surface adsorption sites on strong selective adsorption can be studied. Furthermore, one can study the combined effects of the polydispersity in both q and d on strong selective adsorption, following previous work on weak selective adsorption of random copolymers onto a pattern-recognition surface.[27–29]

In conclusion, our scaling theory of strong selective adsorption emphasizes the critical role of the ratio of the distance between neighboring sticky monomers along the chain to the spacing between neighboring surface adsorption sites, thereby providing a pathway to control the structural characteristics of the adsorption layer, such as the layer thickness and monomer distribution profile, and also the adsorbed amount of polymers, regardless of the specific mechanism for strong binding. As an extension of our theory, one can study the strong selective adsorption of polymers onto nonplanar surfaces. Such an adsorption onto a spherical surface is a relevant model of the adsorption of polyelectrolytes onto nanoparticles with complementary charges, which is essential to the fabrication of nanoparticle polyelectrolyte composites.[18] Furthermore, our scaling theory can be generalized to investigate the strong selective binding between polymer chains with complementary groups, which would hopefully provide an understanding of the various complexes formed between polyelectrolytes or biopolymers.

Supplementary Material

Refer to Web version on PubMed Central for supplementary material.

Acknowledgments

We thank Ekaterina B. Zhulina for valuable comments and suggestions and Nicholas B. Tito for helpful discussions. We acknowledge financial support from the National Science Foundation under Grants DMR-1309892, DMR-1436201, and DMR-1121107, the National Institutes of Health under P01-HL108808 and 1UH2HL123645, and the Cystic Fibrosis Foundation.

References

1. Fleer, GJ.; Stuart, MAC.; Scheutijens, JMHM.; Cosgrove, T.; Vincent, B. Polymers at Interfaces. Chapman and Hall; London: 1993.
2. de Gennes PG. J Phys (Paris). 1976; 37:1445–1452.
3. Scheutjens JMHM, Fleer GJ. J Phys Chem. 1979; 83:1619.
4. Scheutjens JMHM, Fleer GJ. J Phys Chem. 1980; 84:178–190.
5. de Gennes PG. Macromolecules. 1981; 14:1637–1644.
6. Auvray L. Macromolecules. 1987; 20:202–207.
7. de Gennes PG. Adv Colloid Interface Sci. 1987; 27:189–209.
8. Bouchaud E, Daoud M. J Phys (Paris). 1987; 48:1991–2000.
9. Semenov AN, Joanny J-F. Europhys Lett. 1995; 29:279–284.
10. Alexander S. J Phys (Paris). 1977; 38:983–987.
11. de Gennes PG. Macromolecules. 1980; 13:1069–1075.
12. Ou-Yang HD, Gao Z. J Phys II. 1991; 1:1375–1385.
13. Ligoure C. J Phys II. 1993; 3:1607–1617.

14. Aubouy M, Guiselin O, Raphaël E. Macromolecules. 1996; 29:7261–7268.
15. Dobrynin AV, Deshkovski A, Rubinstein M. Macromolecules. 2001; 34:3421–3436.
16. Muthukumar M. J Chem Phys. 1995; 103:4723–4731.
17. Muthukumar M. Proc Natl Acad Sci U S A. 1999; 96:11690–11692. [PubMed: 10518509]
18. Decher, G.; Schlenhoff, JB. Multilayer Thin Films: Sequential Assembly of Nanocomposite Materials. Wiley; Weinheim, Germany: 2003.
19. Lefaux CJ, Zimberlin JA, Dobrynin AV, Mather PT. J Polym Sci, Part B: Polym Phys. 2004; 42:3654–3666.
20. Ravoo BJ, Jacquier JC, Wenz G. Angew Chem, Int Ed. 2003; 42:2066–2070.
21. Crespo-Biel O, Péter M, Bruinink CM, Ravoo BJ, Reinhoudt DN, Huskens J. Chem—Eur J. 2005; 11:2426–2432. [PubMed: 15669046]
22. Wolny PM, Banerji S, Gounou C, Brisson AR, Day AJ, Jackson DG, Richter RP. J Biol Chem. 2010; 285:30170–30180. [PubMed: 20663884]
23. Fasting C, Schalley CA, Weber M, Seitz O, Hecht S, Koksch B, Dernedde J, Graf C, Knapp E-W, Hagg R. Angew Chem, Int Ed. 2012; 51:10472–10498.
24. Dubacheva GV, Curk T, Mognetti BM, Auzely-Velty R, Frenkel D, Richter RP. J Am Chem Soc. 2014; 136:1722–1725. [PubMed: 24400591]
25. Marques CM, Joanny JF. Macromolecules. 1990; 23:268–276.
26. van der Linden CC, van Lent B, Leermakers FAM, Fleer G. J Macromolecules. 1994; 27:1915–1921.
27. Chakraborty AK, Bratko D. J Chem Phys. 1998; 108:1676–1682.
28. Golumbfskie AJ, Pande VS, Chakraborty AK. Proc Natl Acad Sci U S A. 1999; 96:11707–11712. [PubMed: 10518514]
29. Jayaraman A, Hall CK, Genzer J. Phys Rev Lett. 2005; 94:078103. [PubMed: 15783859]
30. Eisenriegler E, Kremer K, Binder K. J Chem Phys. 1982; 77:6296–6320.
31. Eisenriegler, E. Polymers Near Surfaces. World Scientific; Singapore: 1993.
32. Rubinstein, M.; Colby, RH. Polymer Physics. Oxford University Press; Oxford: 2003.
33. Masel, RI. Principles of Adsorption and Reaction on Solid Surfaces. Wiley-Interscience; New York: 1996.
34. Duplantier B. J Phys A. 1986; 19:L1009–L1014.
35. Duplantier B. J Stat Phys. 1989; 54:581–680.
36. This brush layer is absent in the case of weak adsorption with $\delta < 1$.
37. Tito NB, Frenkel D. Macromolecules. 2014; 47:7496–7509. [PubMed: 25400296]

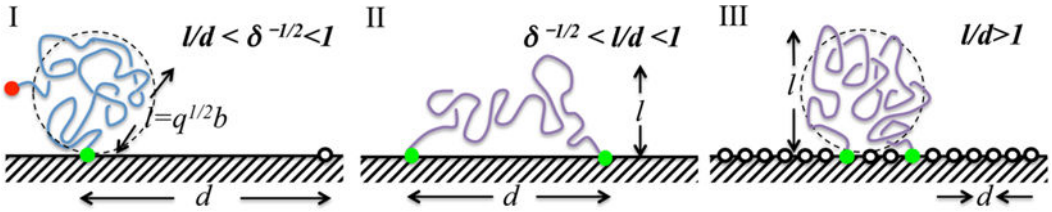


Figure 1.

Schematic sketch of the conformations of a single adsorbed telechelic polymer in different regimes. Green and red filled circles indicate the adsorbed and unadsorbed sticky monomers, respectively. Black empty circles indicate the unoccupied adsorption sites on the surface. This convention of symbols is also used in other figures.

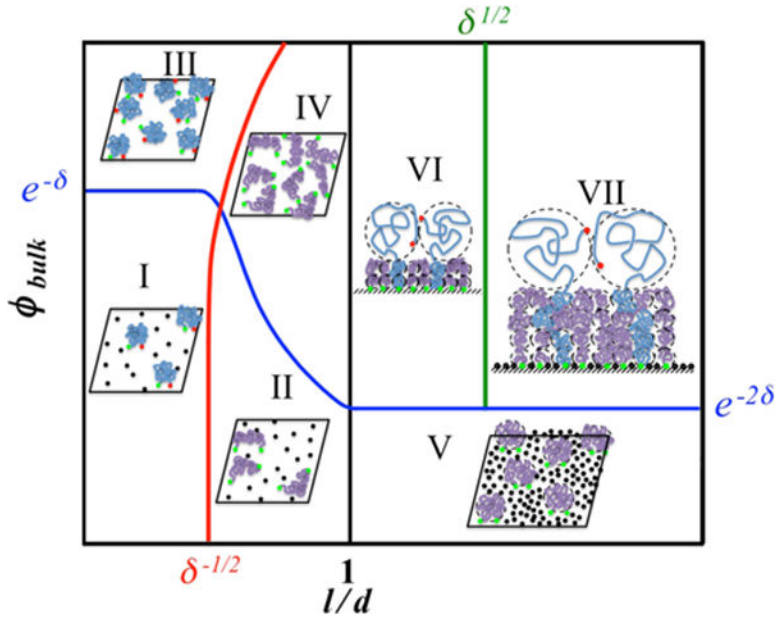


Figure 2.

Diagram for selective adsorption of telechelic polymers. The horizontal axis is the ratio l/d of the size l of unperturbed telechelic chains and the spacing d between neighboring adsorption sites. The vertical axis is the volume fraction φ_{bulk} of polymers in the bulk solution. Both axes are logarithmic. This diagram was drawn for adsorption strength $\delta = 10$ and scaling exponent $\nu = 1/2$. However, it qualitatively captures the general characteristics of such a diagram for any strong selective adsorption with $\delta \gg 1$ of telechelic polymers either in a theta solvent with $\nu = 1/2$ or in a good solvent with $\nu \approx 0.588$.

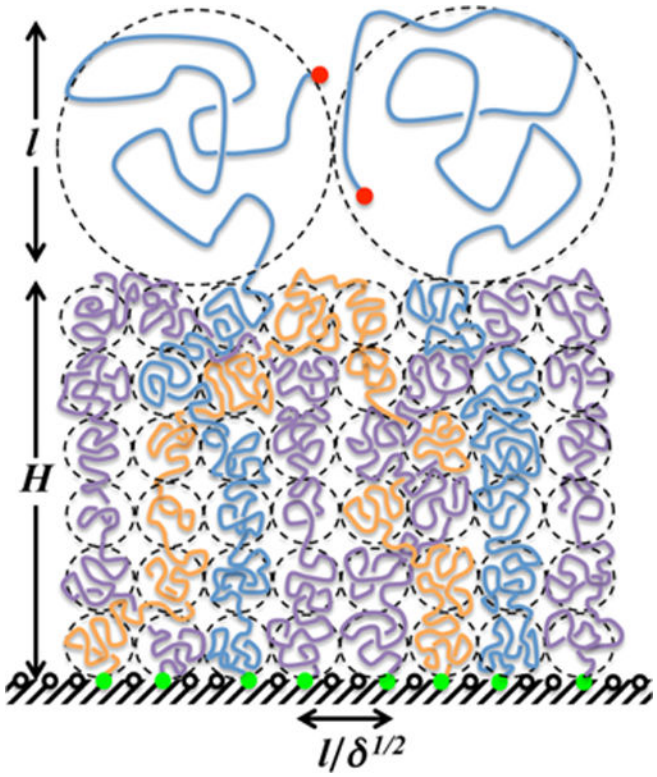


Figure 3.

Schematic sketch of adsorbed telechelic polymers for $l/d > \delta^{1/2}$ at high φ_{bulk}. Violet and orange chains are extended loops fully embedded in the brush layer, while cyan chains have open tails above the brush. The correlation length in the brush layer $\xi \approx l/\delta^{1/2}$, and the height of the brush layer $H \approx l\delta^{1/2}$.

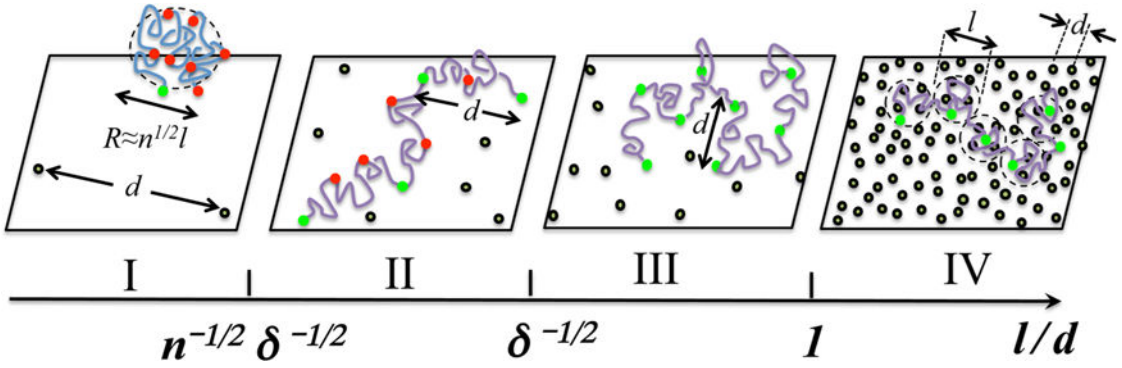


Figure 4.

Schematic sketch of the conformation of an adsorbed multisticker polymer in different regimes.

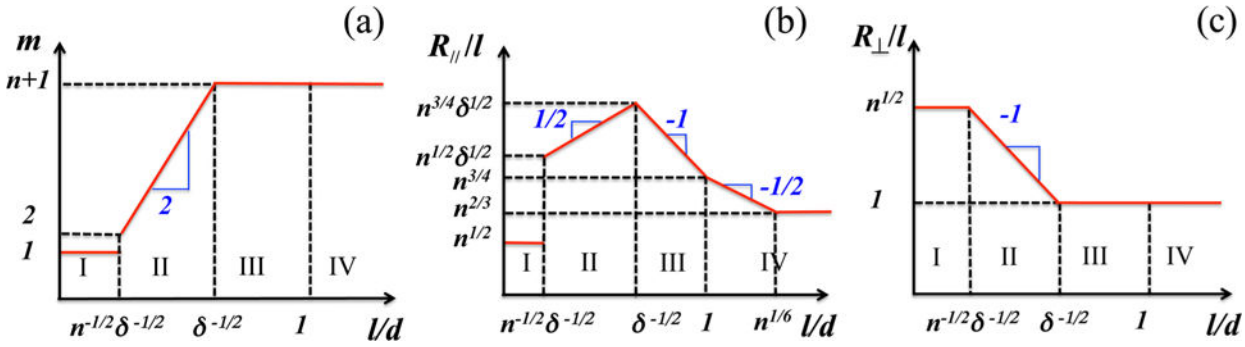


Figure 5.

Adsorption of a single multisticker polymer. Dependence of (a) the number m of adsorbed sticky monomers per chain, (b) the size $R_{\parallel}$ of the adsorbed chain along the adsorption surface normalized by the unperturbed size l of linking segments, and (c) the chain size $R_{\perp}$ perpendicular to the surface normalized by the size l on the ratio l/d, where d is the average distance between neighboring adsorption sites on the surface. Logarithmic scales.

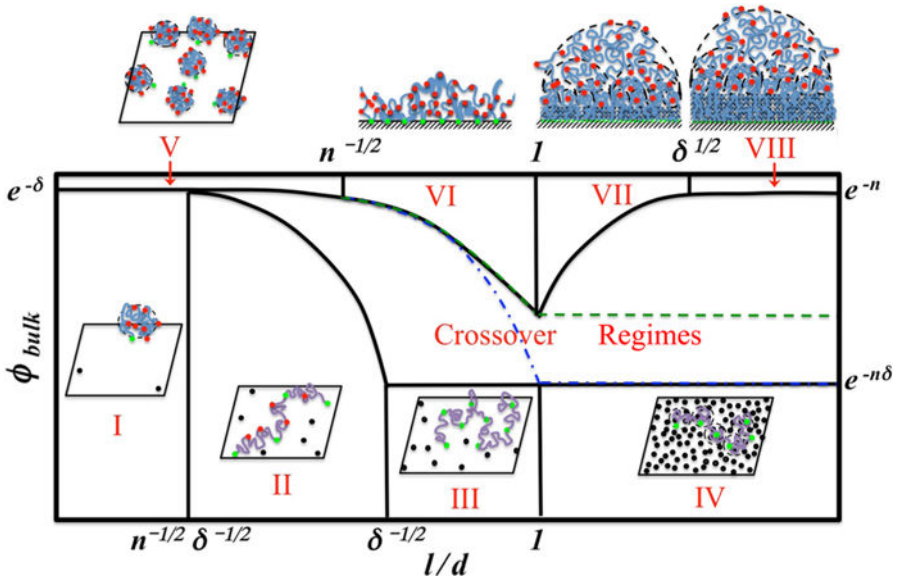


Figure 6.

Selective adsorption diagram of multisticker polymers as a function of l/d, the ratio of the distance l between neighboring sticky monomers along the unperturbed chain and the spacing d between neighboring adsorption sites on the surface. The vertical axis is the volume fraction φ_{bulk} of polymers in the bulk solution. Both axes are logarithmic. In the crossover regimes, the blue dash-dotted line indicates the bulk volume fraction $\phi_{\text{bulk}}^{\text{unstretched}}$ at which the adsorbed chains become unstretched, while the green dashed line indicates the bulk volume fraction $\phi_{\text{bulk}}^{\text{carpet}}$ at which the self-similar carpet is fully developed. The adsorption strength per sticker $\delta = 10$, the number of sticky monomers per chain $n = 20$, and the scaling exponent $\nu = 1/2$ for theta solvent were used to draw the diagram. However, the generic features of the diagram for strong selective adsorption of multisticker polymers with $\delta \gg 1$ and $n \gg 1$ in either a theta solvent with $\nu = 1/2$ or a good solvent with $\nu \approx 0.588$ are the same.

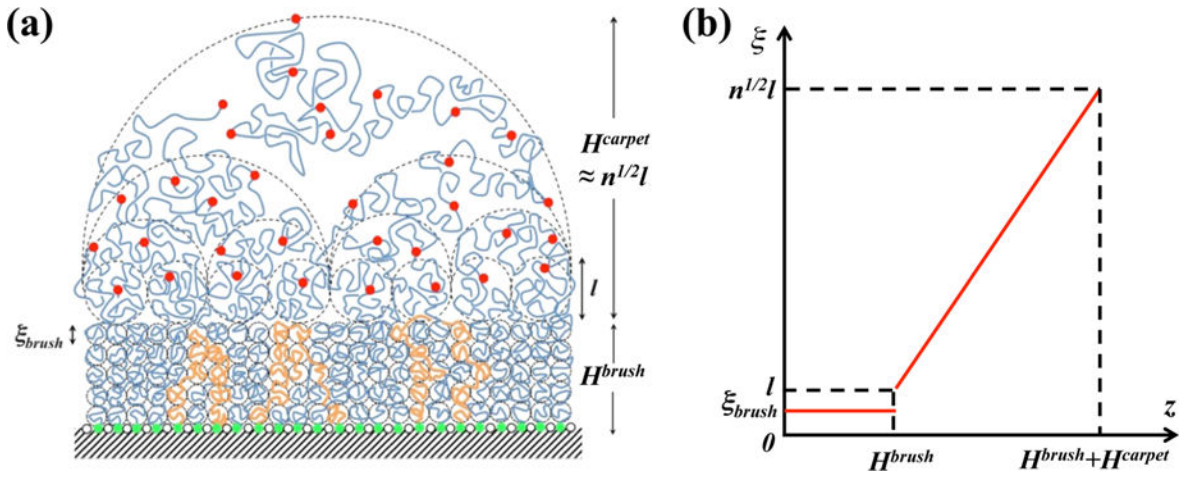


Figure 7.

(a) Schematic sketch of adsorbed multisticker polymers for $l/d > 1$ at high φ_{bulk}. Dashed lines indicate the correlation blobs. The size of correlations blobs is ξbrush in the brush layer. In the carpet layer, the correlation blob size increases from the size l of linking segments at distance $\approx l$ above the brush to the ideal polymer size $n^{1/2}l$ at height $\approx n^{1/2}l$ above the brush. Three loops in the brush layer formed by extended linking segments bound to the adsorption surface are highlighted in orange. (b) Dependence of the correlation blob size ξ on the distance z from the adsorption surface (linear scales). The smallest correlation blob size is $\xi_{brush} \approx d$ in regime VII while $\xi_{brush} \approx l/\delta^{1/2}$ in regime VIII.

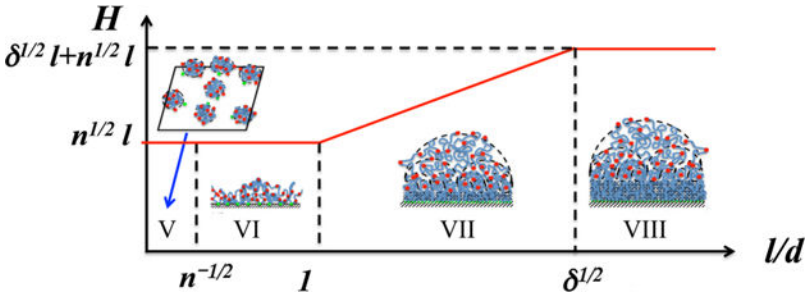


Figure 8.

Thickness H of the layer of adsorbed multisticker polymers as a function of the ratio l/d at a constant relatively high polymer volume fraction $\varphi_{bulk} > e^{-\delta}$ (linear scales).

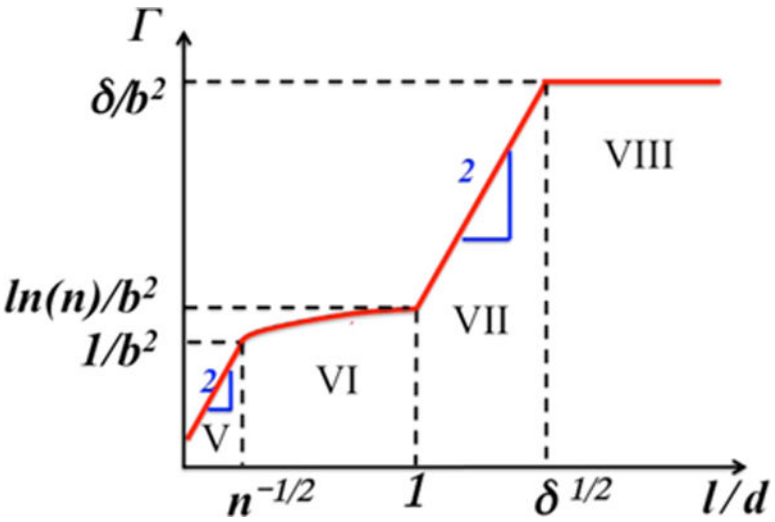


Figure 9.

Dependence of the adsorbed amount Γ of multisticker polymers per unit area on *l*/d, at a constant relatively high polymer volume fraction ($\varphi_{bulk} > e^{-\delta}$ if $n > \delta$ and $\varphi_{bulk} > e^{-n}$ if $n < \delta$). Logarithmic scales.